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Molecular structure and thermodynamic properties of the gaseous ThC_2 and ThC_4 species

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Abstract

The geometry and vibrations of the ThC_2 and ThC_4 molecules have been derived from quantum chemical calculations. The results indicate an asymmetric L-type structure for ThC_2 and a planar fan-type structure for ThC_4, in contrast to the linear structures assumed earlier. The entropies of ThC_2 and ThC_4 calculated from the results are compared to 'experimental' values derived from existing vaporisation studies.

1. Introduction

It has been shown experimentally that a large variety of binary molecules exists in the vapour above the actinide carbides, in addition to the atomic An(g) and molecular C_n species. Mass spectrometric studies of the Th-C system by Jackson et al. [1], Sasaki et al. [2], Kohl and Stearns [3] and Gingerich [4] revealed the presence of ThC_n species up to $n = 4$, whereas Gupta and Gingerich [5] also detected the ThC_5 and ThC_6 species in the vapour. Similar observations have been made for the U–C system [6–8,4]. The partial pressures of the species in the vapour differ strongly and only the AnC_2 and the AnC_4 species have significant contributions to the total vapour pressure.

In the above mentioned studies the experimental data were analysed by second- and third-law methods using estimated thermal functions. Since no structural or spectroscopic data were available for these species it was assumed by all the research teams that the AnC_2 and AnC_4 molecules have C–C–An and C–C–An–C–C linear structures. However, recent quantum chemical calculations for the lanthanum carbides by Roszak and Balasubramanian [9] indicated that LaC_2 has a cyclic (or 'fan') structure. Similar results have been reported for the LaC_2^+ ion [10]. This raises the question whether the gaseous actinide carbide species also have cyclic structures. To investigate this we have performed quantum-chemical calculations for the ThC_2 and ThC_4 molecules, of which the results are presented here.

2. Method of calculation

The geometry and vibrational frequencies of the ThC_2 and ThC_4 molecules have been computed using state-of-the-art quantum chemical methods [11]. The computations have been performed using the second-order Møller–Plesset perturbation theory (MP2) [12] in conjunction with a small-core (60 e) quasi-relativistic effective core potential (ECP) for thorium augmented with a [12s, 11p, 10d, 8f/8s, 7p, 6d, 4f] contracted valence basis set treating explicitly the 5, 6 and 7 shells [13–15]. Recent studies for uranium(VI) compounds demonstrated the superiority of this small-core ECP with respect to the large-core (78 e) one [14] treating explicitly the 5f, 6s, 6p, 6d and 7s electrons only [16–18]. For carbon the correlation consistent

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aug–cc–pVTZ basis [15,19] was used except for the assessment of the anharmonic effects on the normal modes. Because of the considerably larger computational costs to evaluate a fourth-order force field, we applied here the aug–cc–pVDZ [19] basis for carbon. The calculations were carried out with the Gaussian03 program package [20]. The computed geometries and normal modes have been visualised using the GaussView 3.09 program.

3. Results and discussion

According to a recent comprehensive computational study of ThO, the Th^{2+} ion has a singlet ground state in that molecule [21]. On the basis of this we also expected that the singlet states of ThC_2 and ThC_4 are more stable than the triplet states. To justify this expectation, we performed a detailed study of various structures on the triplet potential energy surface of ThC_2. Computing the triplet linear C_{∞}, symmetric C_{2v} and asymmetric L-type C_s structures revealed the C_s as the most stable triplet structure, but still being higher in energy by 53.4 kJ mol^{-1} than the most stable singlet one (*vide infra*).

The computed structures for the singlet states of ThC_2 and ThC_4 are presented in Fig. 1. In contrast to the results for LaC_2 by Roszak and Balasubramanian [9], who reported the C_{2v} structure as the most stable, we found the asymmetric L-type C_s structure as the global minimum for ThC_2. The C_{2v} structure is a somewhat higher lying (by 7.7 kJ mol^{-1}) first-order saddle-point on the potential energy surface of ThC_2. The previously assumed linear Th–C–C arrangement is another saddle-point with two imaginary frequencies. The calculated most stable structure of ThC_4 is analogous to that of LaC_4 [22]. This fan-type planar C_{2v} arrangement is more stable by 38 kJ mol^{-1} compared to the non-planar C_2 one (both can be derived from the C_s structure of ThC_2). The computed geometrical parameters and vibrational frequencies are compiled in Table 1. The computed natural atomic charges reveal a considerable charge transfer in ThC_4 from the carbene anions to Th^{4+}, resulting in an effective charge of +1.66 in the global minimum structure. The charge transfer is much less in ThC_2, where the formally Th^{2+} ion has an effective charge of +1.60 in the most stable C_s structure.

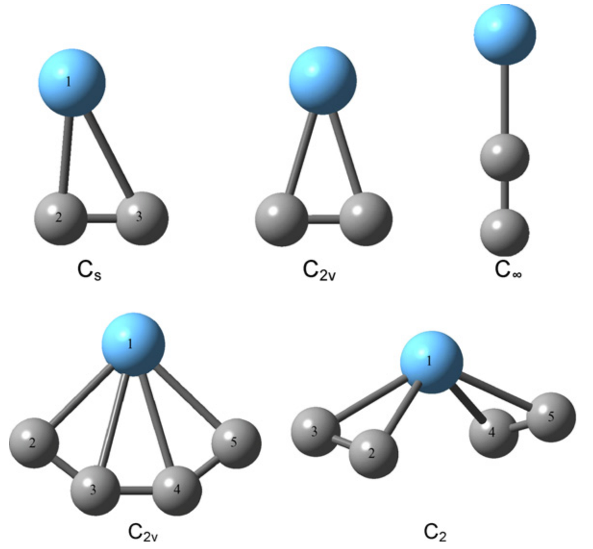

Fig. 1. Optimized structures for ThC_2 and ThC_4 and numbering of atoms.

From the results we have calculated the thermodynamic functions of ThC_2 and ThC_4 using a rigid rotor harmonic oscillator approximation. For the calculations of the electronic contributions we have estimated the electronic energy levels to be identical to ThO(g). The results can be compared to the thermodynamic functions calculated for the linear molecular structures by other authors [1,3,5] in the past, as is shown in Table 2. The difference principally arises from the rotational contribution, which is higher in case of the fan-shaped structure, and the vibrational contribution, which is substantially lower in case of the fan-shaped structure, but only partially compensate.

The calculated entropies of the ThC_2 and ThC_4 molecules can be compared to the second-law entropies derived from the mass spectrometric studies. Jackson et al. [1] studied the reaction

$$ThC_2(cr) = ThC_2(g), \qquad (1)$$

assuming the stoichiometric composition for the solid phase, which does not exist. According to the phase diagram [23] the limiting composition of the ThC_{2-x} phase at the temperatures of the experiments is $ThC_{1.96}$. With the same assumption we derive at the mean temperature of

Table 1
Computed geometrical parameters (pm, deg.) and anharmonic vibrational frequencies (cm^{-1}) of most favourable structures of ThC_2 and ThC_4[a]

Parameter[b]	ThC_2	ThC_4
	C_s	C_{2v}
r(Th–C_2)	215.5	236.5
r(Th–C_3)	247.3	253.2
r(C_2–C_3)	128.7	128.5
r(C_3–C_4)		136.3
∠(Th–C_2–C_3)	88.1	82.1
∠(Th–C_3–C_2)	60.6	67.7
∠(C_2–Th–C_3)	31.3	30.2
∠(C_3–Th–C_4)		31.2
∠(Th–C_3–C_4)		74.4
νC–C $+\delta$	1649 (1674)	1761 (1818)
		1632 (1706)
		1051 (1054)
νTh–C $+\delta$	616 (632)	637 (642)
	197 (210)	440 (474)
		388 (393)
		363 (372)
γ		509 (499)
		277 (280)

[a] The harmonic frequencies (in parenthesis) were computed using the aug–cc–pVTZ basis set for carbon. The anharmonic frequencies were derived from these values using anharmonic corrections from computations with aug–cc–pVDZ basis set for carbon.

[b] The abbreviations ν, δ and γ mean stretching, deformation and wagging vibrations, respectively.

Table 2
The calculated free energy function $-\{G°(T) - H°(298.15\ \mathrm{K})\}/T$ of the ThC_2 and ThC_4 molecules

	T/K	[1]	[3]	[5]	This study
ThC_2	298.15		257.1	270.7	286.0
	2500	327.01	323.9	346.4	351.4
ThC_4	298.15		294.3	289.9	306.9
	2500		410.6	406.0	419.4

their experiment $S°(ThC_2, g, 2500\ K) = 384.1\ J\ K^{-1}\ mol^{-1}$ using the estimated heat capacity data for the solid from Holley et al. [23], compared to $404.1\ J\ K^{-1}\ mol^{-1}$ calculated from the present molecular data. Kohl and Stearns [3] studied the same reaction and from their results we obtain at the mean temperature of the experiment $S°(ThC_2, g, 2792\ K) = 428\ J\ K^{-1}\ mol^{-1}$. The results of these authors also allow to analyse the reaction

$$Th(g) + 2C(cr) = ThC_2(g), \qquad (2)$$

from which we derive $S°(ThC_2, g, 2792\ K) = 384.0\ J\ K^{-1}\ mol^{-1}$, assuming the activity of carbon to be unity and using the well-known data for Th(g) and C(cr) [24]. The latter two 'experimental' entropies can be compared to the calculated value of $412.4\ J\ K^{-1}\ mol^{-1}$ at $T = 2792$ K; the agreement being reasonable for the average ($406\ J\ K^{-1}\ mol^{-1}$) but not for the individual values.

It is clear that these 'experimental' entropy values themselves are not consistent. Firstly there is an evident difference between the two routes within one experimental determination [3], very likely related to the auxiliary data (ThC_2) and assumptions made. Secondly the solid phase phase composition could have been different in the two studies, as the ThC_{2-x} phase has a wide composition range. This is supported by the fact that the measured ThC_2^+/Th^+ ion-intensity ratio is appreciably different in the two studies.

In the same way we derive from the results of Kohl and Stearns [3] $S°(ThC_4, g, 2792\ K) = 540.5\ J\ K^{-1}\ mol^{-1}$ from the reaction $Th(g) + 4C(cr) = ThC_4(g)$ compared to $524.7\ J\ K^{-1}\ mol^{-1}$ calculated. The agreement is not very good, but considerably better than found by Kohl and Stearns [3] for a linear ThC_4 molecule.

We can conclude that the quantum chemical computations clearly indicate that the ThC_2 and ThC_4 molecules have cyclic structures, and not linear structures as assumed in the past. The thermodynamic functions of gaseous ThC_2 and ThC_4 derived from the computed molecular properties differ considerably from the earlier estimates for linear molecules. However, the agreement of the calculated entropies with the values derived from the experimental mass spectrometric data is only marginally improved, which is due to the fact that the experimental results are not accurate enough to draw firm conclusions.

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